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14. ABSTRACT This DURIP grant was used to purchase: 1. Q600 SDT Simultaneous DSC-TGA 2. Pfeiffer Vacuum Benchtop Thermostar Mass Spectrometer 3. Vision Research Phantom V12.1-8G-M high speed camera					
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Report Title

Final Report: Measurement System for Energetic Materials Decomposition

ABSTRACT

This DURIP grant was used to purchase:

1. Q600 SDT Simultaneous DSC-TGA
2. Pfeiffer Vacuum Benchtop Thermostar Mass Spectrometer
3. Vision Research Phantom V12.1-8G-M high speed camera

These instruments have been used to evaluate and study decomposition and reactivity of energetic materials

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received

Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received

Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT_SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Names of Under Graduate students supported

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

"see Attachment"

Technology Transfer

DURIP Program Final Report W911NF1210358

Measurement System for Energetic Materials Decomposition

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Background

Energetic materials have been utilized for both civil and military applications for many years. Traditionally, energetic materials are considered to range from slow burning propellants to detonating high-nitrogen explosives which contain both the fuel and oxidizer intermixed at the molecular scale (i.e. TNT, RDX, etc.). A third class of energetic materials termed Metastable Intermolecular Composites, or MICs, has been developed more recently [Au95]. These formulations typically contain fuel and oxidizer nanoparticles which have been intimately mixed in order to dramatically reduce mass transfer limitations. Aluminum is primarily used as the fuel due to a combination of its energy density and abundance, while a variety of oxidizers have been studied, including CuO, Bi₂O₃, MoO₃, WO₃, AgIO₃, etc.

Instruments Purchased

This DURIP grant enabled purchase of two instruments to enhance our lab at UMD to study decomposition and reactivity of both MIC's and molecular energetics.

1. TGA/DSC/Mass spectrometer

Our laboratory was lacking the capability to probe slow chemistry and initiation mechanisms. The proposal sought funds to purchase a thermal analysis system which included thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and differential thermal analysis (DTA). In addition the system was to be integrated with a mass spectrometer. One key advantage of thermal analysis is that results can be obtained using a sample size on the order of milligrams. This is advantageous not only for safety reasons, but also because our lab is equipped with several methods for small-scale nanoparticle generation via aerosol methods, and having thermal analysis available would provide excellent synergy with our existing equipment. We are capable of generating small amounts of many different types of nanoparticles with unique compositions and morphologies, and thermal/gas analysis will be highly useful in studying their decomposition behavior and evaluating the performance of new types of oxidizers.

Instrument Specifications and Sample Results

A Q600 SDT – Pfeiffer MS thermal analysis system that couples a thermogravimetric analyzer, differential scanning calorimeter and integrated mass spectrometer was purchased in December, 2012 and received in February, 2013.

Q600 SDT Simultaneous DSC-TGA: Provides a true simultaneous measurement of heat flow (DSC) and weight change (TGA) on the same sample from ambient to 1,500 deg. C. DSC noise is <4 microwatts and the TGA balance sensitivity is 0.1 microgram. A heat flux DSC design with separate sample and reference pans is used, and is calibrated for heat flow measurements using sapphire. The Q600 features automated furnace movement and a horizontal purge gas system with digital mass flow controllers and programmable gas switching capability. A separate Inconel 600 tube permits introduction of reactive gases into the sample chamber. The Q600 design allows evolved gas studies using FTIR or MS.

Pfeiffer Vacuum Benchtop Thermostar Mass Spectrometer (110/220V): For analysis of all gases evolved during thermogravimetric analysis experiments. It includes Quadera Software, heated capillary interface, and calibration device with perfluorotributylamine (PFTBA). The MS offers multiple ion detection capability and has a range of 1 -300 amu.



Figure 1: TGA/DCS/MS system now located at UMD.

This equipment has been used to provide the university with valuable insight into the thermal ignition mechanism of materials. For example in Figure 2 and Figure 3 are TGA and DSC plots of a sample material-homemade $K_2S_2O_8$, while Figure 4 is O_2 MS signal of the same sample. The integrated system enables the university to evaluate new

types of energetic materials, and aided the university to further develop and understand new and more efficient oxidizers for nanocomposites systems.

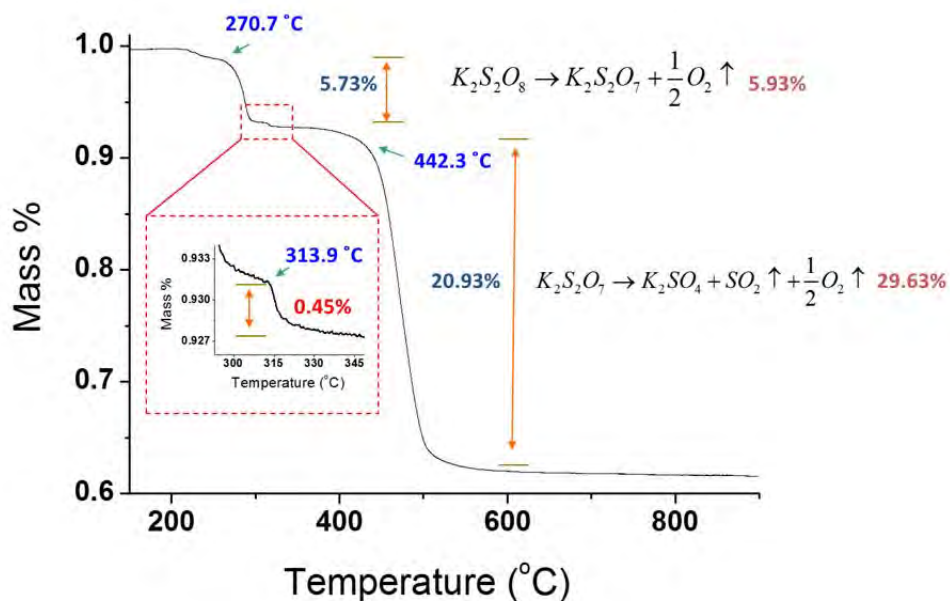


Figure 2. TGA data of synthesized $K_2S_2O_8$

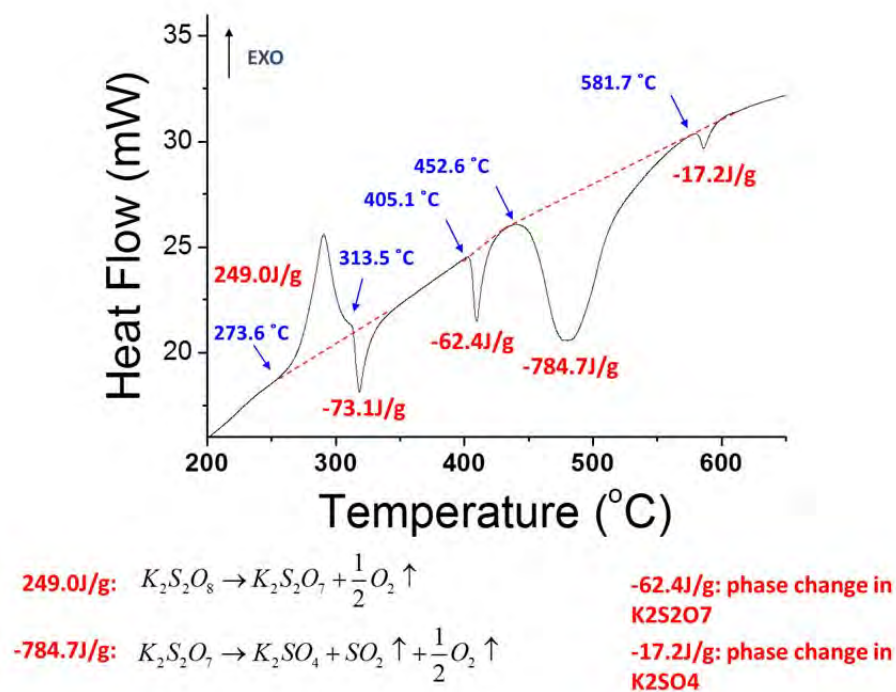


Figure 3. DSC data of synthesized $K_2S_2O_8$

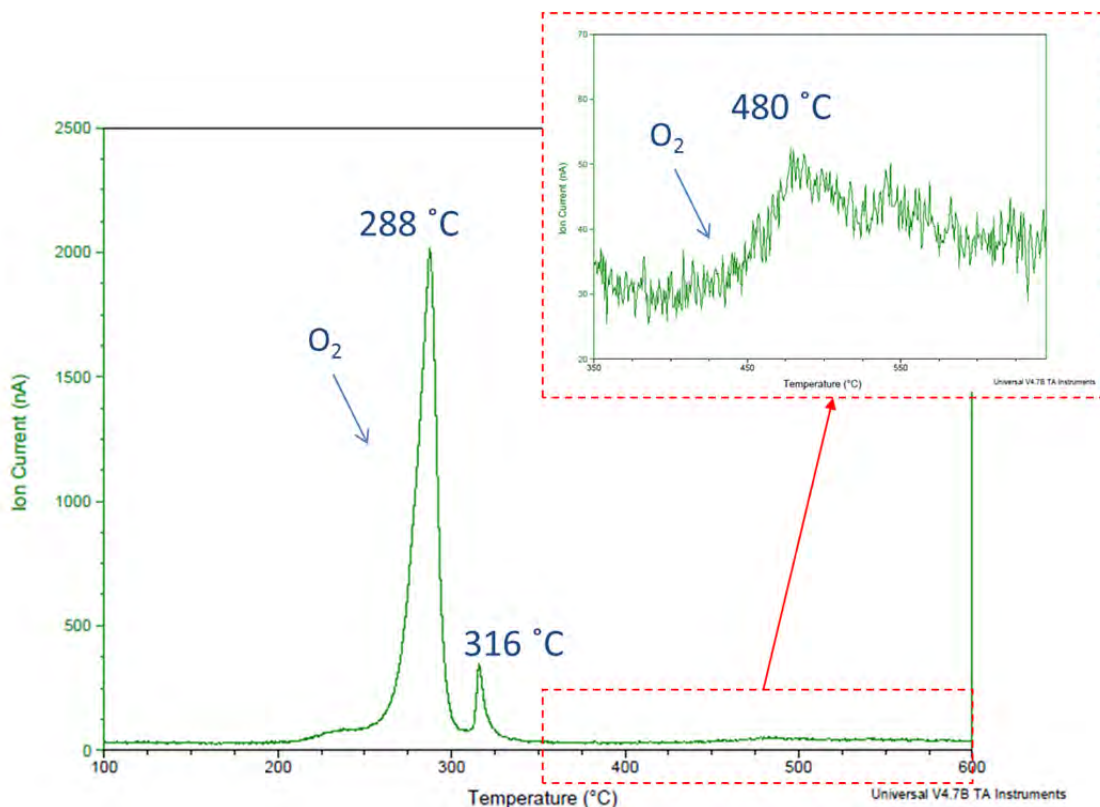


Figure 4. TGA-MS O_2 signal of homemade $K_2S_2O_8$

2. High Speed Imaging Camera

Our laboratory was lacking any high speed imaging capability which was needed for understanding visually the nature of our highly reactive systems.

Instrument Specifications and Sample Results

Vision Research Phantom V12.1-8G-M

Our Phantom V12.1 is a 1 megapixel monochromatic digital high-speed camera capable of taking more than 6242 frames-per-second (fps) at full 1280 x 800 resolution and 1000000 fps at reduced resolution (128 x 8 pixels). The camera also boasts a wide aspect ratio (1280 x 800 CMOS sensor), high light sensitivity (active pixel size of 20 microns), a sub-microsecond shutter capability (minimum 300 ns in 18ns intervals), 12-bit pixel depth, and 10GB of on-board memory.

The camera has been used for a wide variety of projects involving nanoparticle burning and thermites. Several examples are illustrated below:

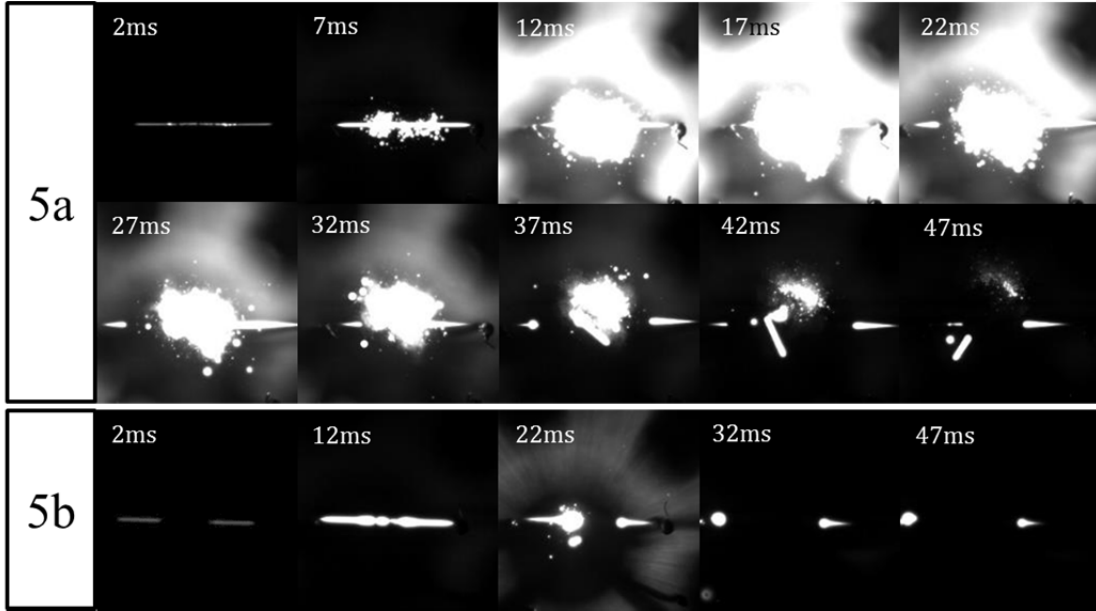


Figure 5. High speed video images: (a): Gelled aluminum microparticles; (b) Nanoaluminum The labeled numbers are time elapsed after triggering.



Figure 6. Temporal video snapshots of Al/CuO nanothermite combustion on a 76 micron Pt wire, Heating rate = $\sim 2 \times 10^5$ K/s, time(μs) measured from the start of ignition.

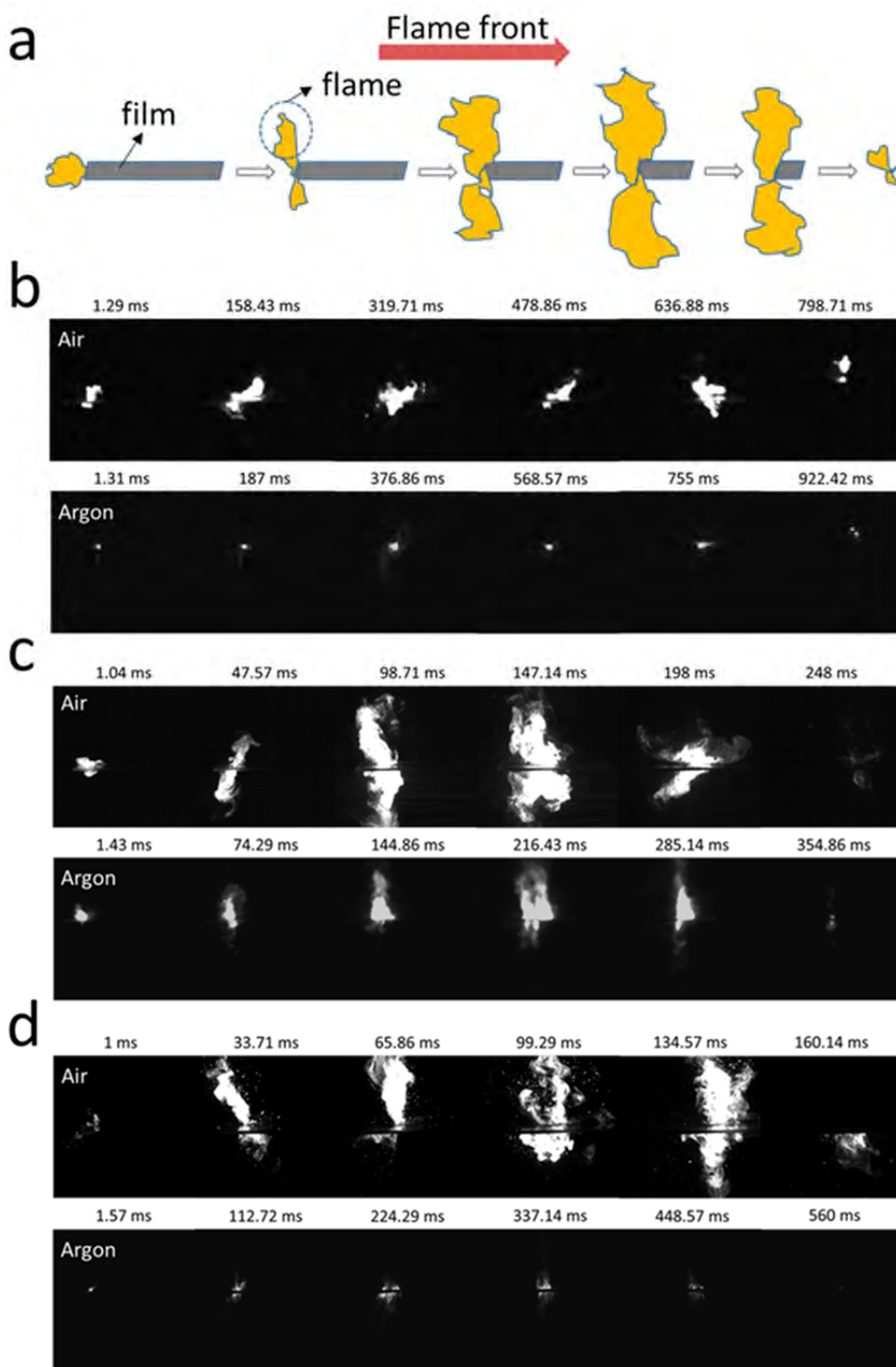


Figure 7 (a) Schematic showing of flame propagation. (b - d) Selected frames of Al/PVDF films combustion using high speed camera, with loading 16.7, 30, 50 wt% Al-NPs, respectively. Note: The time stamps on the top of each picture indicated elapsed time from the starting trigger.

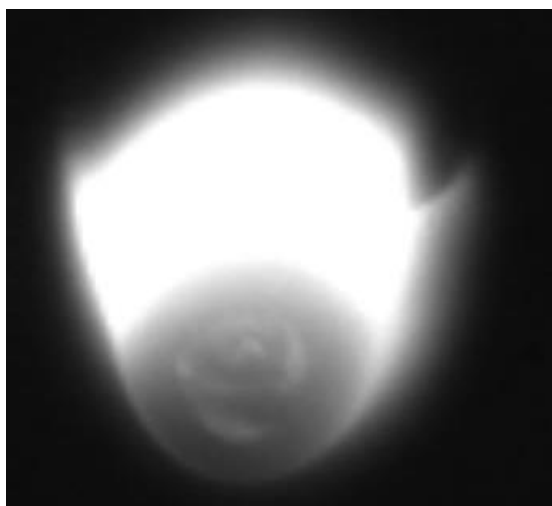


Figure 7. Droplet of toluene containing [Al-Br-N-Et₃]₄ cluster showing enhanced burning rate and gas generation within droplet.